Porous, Single Crystalline Titanium Nitride Nanoplates Grown on Carbon Fibers: an Excellent Counter Electrode for Low-cost, High Performance, Fiber-shaped Dye-Sensitized Solar Cells

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Supporting Information

Experimental

Fabrication of TiO_2 and TiN Nanoplates on carbon fibers (CF): The TiO_2 nanoplates grown on CF by a hydrothermal method.[1] A bound of commercial CF was ultrasonically cleaned in ethanol for 30 min. 0.25 g ammonium hexafluorotitanate was added to the mixture solvent containing 15 mL deionized water, 15mL hydrochloric acid, and 0.5mL tetrabutyl titanate. After stirring of 30 min, the mixture solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, followed by addition of the clean CF. The sealed autoclave was then put into an electric oven at 180 ºC for 24 h. After reaction, the sealed autoclave cooled down to room temperature naturally. The as-prepared anatase TiO_2 nanoplates arrays on CF (labeled as TiO_2-CF) was taken out and rinsed with deionized water, ethanol and then dried at 60 ºC. Afterward, the synthesized TiO_2-CF was calcined in a tube furnace in ammonia atmosphere at 900 °C. At the beginning of ammonification process, ammonia was flowed into the tube at a rate of 300 sccm for half an hour to expel the air in the tube. While maintaining the flowing ammonia of 150 sccm, the temperature was firstly increased from room temperature to 900 °C at a rate of 10 $°C\cdot min^{-1}$; maintaining the temperature for 1 h afterward. The TiN nanoplates arrays on CF (TiN-CF), which was allowed to cool to room temperature in ammonia atmosphere, was obtained as the sample.

Solar Cell Fabrication: The TiO_2 nanotube arrays-coated Ti thread as a photoanode was prepared with an electrochemical anodization process. A Ti thread (diameter of 250 μm) was treated by electrochemical anodization under constant voltage 60 V and temperature 25 ^oC for 7~8 h in a two-electrodes system. The electrolyte is a mixture of NH_4F (0.2 wt%) and H_2O (1 wt%) in ethylene glycol, and the anode and cathode electrodes are Ti thread and carbon rod, respectively. After being washed with deionized water, the anodized Ti thread annealed at

450℃ in air for 1 h to produce the anatase titania nanotube (as shown in Figure S5, S6b and S6d). The anodized Ti thread was then immersed in 0.2M $TiCl_4$ solution bath at 70 ^oC for 30 min. Afterwards, Ti thread was taken out and sintered for 30 min at 450 ^oC in air. When cooled to 80 ºC, the obtained Ti thread was soaked in 0.5 mM N719 dye solution (solvent alcohol) and kept for 24~48h at room temperature. Here 1.0 M 1–Butyl–3–methylimidazolium iodide (BMIMI), 50 mM LiI, 30 mM I_2 and 0.5 M tert–butylpyridine in a mixed solvent of acetonitrile and 85 valeronitrile (v/v, 85:15) was used as electrolyte. A stick of dye-coated Ti thread and TiN-CF were inserted into a transparent capillary filled with electrolyte in order to assemble into FDSSC.

Characterization: The field emission scanning electron microscopy (FE-SEM) images were obtained on an XL30 ESEM FEG scanning electron microscopy operating at 20 kV. The transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) images were observed on a JEM 200CX TEM instrument. The crystallographic phase of the as-prepared products was determined by powder X-ray diffraction (XRD) (Rigaku Ultima III, Japan) using Cu-Ka radiation (λ=0.154178 nm) with scan rate of 100 min^{-1} at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was collected on an ESCALab MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K X-ray as the excitation source.

Photovoltaic Characterization: Those I–V measurements were carried out, with the length FDSSC of 3 cm, on a Keithley 236 source measurement unit under AM 1.5 illumination cast by an Oriel 92251A-1000 sunlight simulator calibrated by the standard reference of a Newport 91150 silicon solar cell. Electrochemical impedance spectroscopic (EIS) curves of the symmetric cells fabricated with two identical electrodes (CE/electrolyte/CE) were observed by electrochemical analyzer (Solartron 1260+1287) with a 10 mV amplitude perturbation and the frequency range was from 100 mHz to 100 kHz. The symmetric cells fabricated with two identical electrodes (CE/electrolyte/CE) were used to perform the Tafel polarization measurements with PAR2273 workstation. The cyclic voltammetry (CV) measurements were conducted in a three-electrode system at a scan rate of 50 mV·S^{-1} by using PAR2273 workstation (Princeton Applied Research, USA). The counter and reference electrode are Pt and Ag/AgCl composite electrode, respectively. The I_3^-/I^- electrolyte contained 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 in acetonitrile.

References

1. S. L. Feng, J. Y. Yang, H. Zhu, M. Liu, J. S. Zhang, J. Wu and J. Y Wan, *J. Am. Ceram. Soc.*, 2011, **94**, 310

Supplementary Table

Table S1. Comparison with the photoelectrochemical performance of FDSSCs using various counter electrodes.

	Work electrode	Counter electrode	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor	η	Reference
Free-Pt based counter electrode	Ti thread covered TiO_2 nanotube	TiN-carbon fiber	0.64	19.35	0.58	7.20 %	This work
		Pt wire	0.70	12.70	0.70	6.23 %	
	Ti thread covered TiO_2 nanoparticles	Ti-Nitrogen-doped graphene	0.73	10.5	0.71	5.40 %	Ref. 28
		Pt wire	0.71	10.5	0.68	5.10 %	
	Ti thread covered TiO_2 nanotube	Ni-Carbon nanotube fiber	0.73	14.43	0.571	6.04 %	Ref. 4
		Carbon nanotube fiber	0.73	13.99	0.497	5.07 %	
	Ti thread covered TiO_2 nanoparticles	PEDOT-Carbon fiber	0.68	12.01	0.69	5.61 %	Ref. 27
		Pt-Carbon fiber	0.69	11.13	0.67	5.08 %	
Pt based counter electrode	Ti thread covered TiO_2 nanotube	Pt-Graphene	0.73	17.11	0.67	8.41 %	Ref. 18
		Pt wire	0.74	16.35	0.60	7.22 %	
	Ti thread covered TiO_2 nanotube	Pt-Ni-Carbon nanotube fiber	-	-	-	8.03 %	Ref. 4
		Pt wire	-	-	-	6.52 %	
	Ti thread covered TiO_2 nanotube	Pt-Carbon naotube fiber	0.54	15.30	0.59	4.85 %	Ref. 17
		Pt wire	-	-	-	4.23 %	
	Ti thread covered TiO_2 nanoparticles	Pt-Carbon fiber/stainless steel wire	0.68	11.66	0.74	5.85 %	Ref. 16
		Pt-Carbon fiber	0.72	10.55	0.67	5.08 %	
		Pt wire	0.75	8.65	0.73	4.75 %	

Supplementary Figures

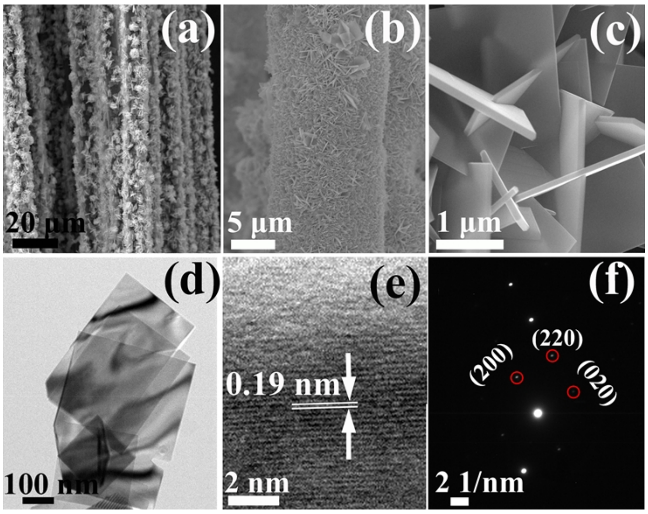

Figure S1. (a), (b) and (c) low magnification and high magnification FE-SEM images of TiO_2 nanoplates, (d) TEM image, (e) HRTEM image, and (f) SAED recorded from TiO_2 nanoplate.

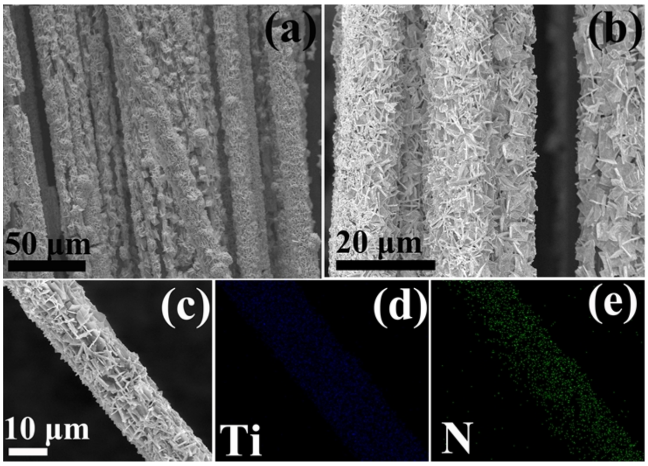

Figure S2. (a), (b), and (c) low magnification and high magnification FE-SEM images of TiN nanoplates; (d) and (e) TiN-CF was characterized using EDX elemental mapping.

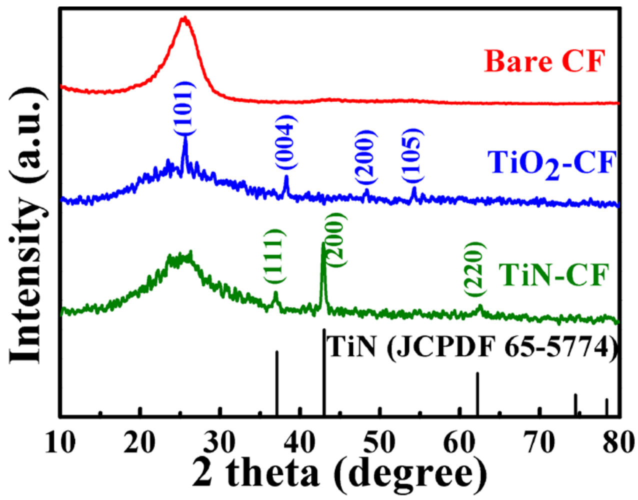

Figure S3. XRD patterns collected from TiN-CF, TiO_2-CF and bare CF.

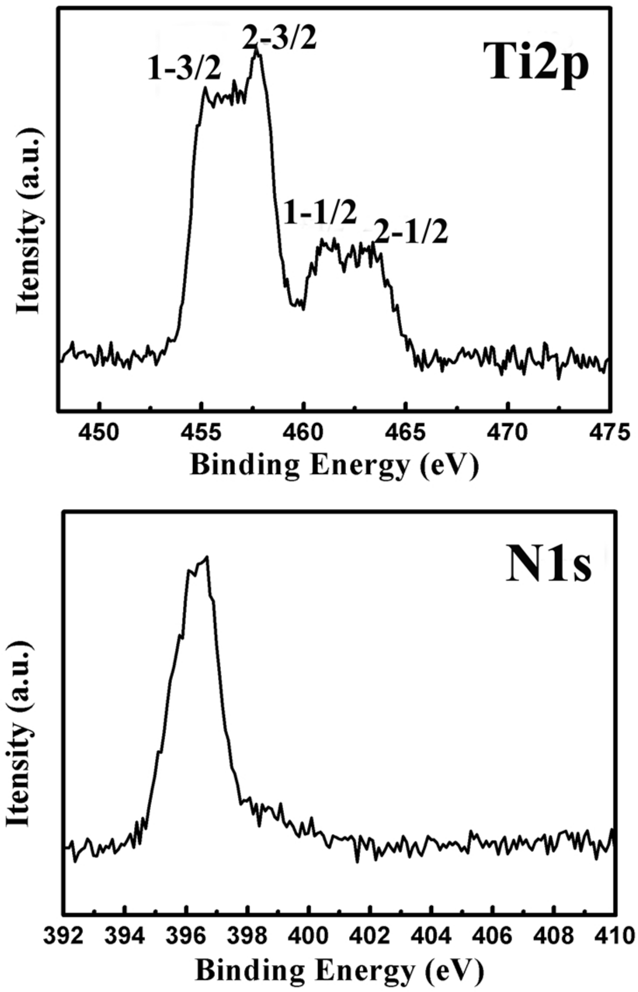

Figure S4. XPS collected from TiN nanoplates.

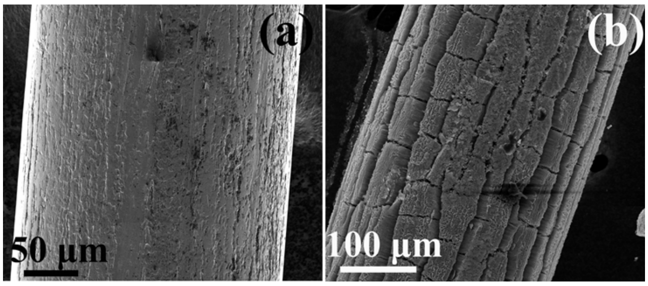

Figure S5. The FE-SEM images of (a) Ti thread, (b) a Ti thread coated with TiO2 nanotube arrays.

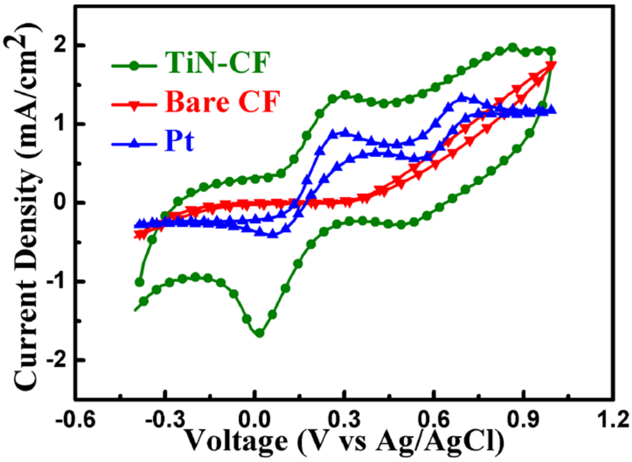

Figure S6. Cyclic voltammograms for TiN-CF, Pt wire electrodes and bare CF.

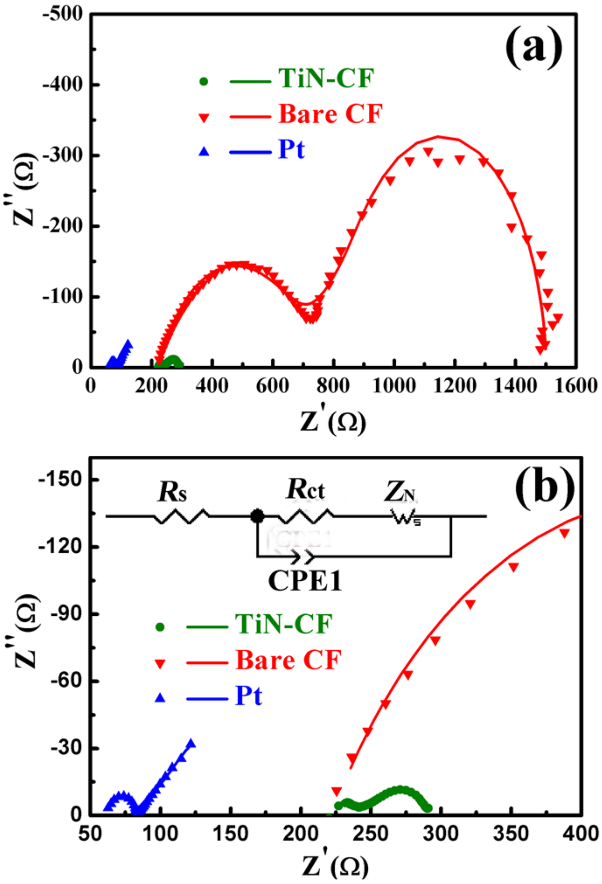

Figure S7. (a) Nyquist plots of the symmetric cells with two identical counter electrodes of TiN-CF, Pt wire or bare CF in the measured frequency range from 100 kHz to 100 mHz. The spectra for both cells were measured in the same redox active electrolyte; (b) the enlargement of (a). The symbols are experimental data, and the solid lines are fitted results according to the inset equivalent circuit.

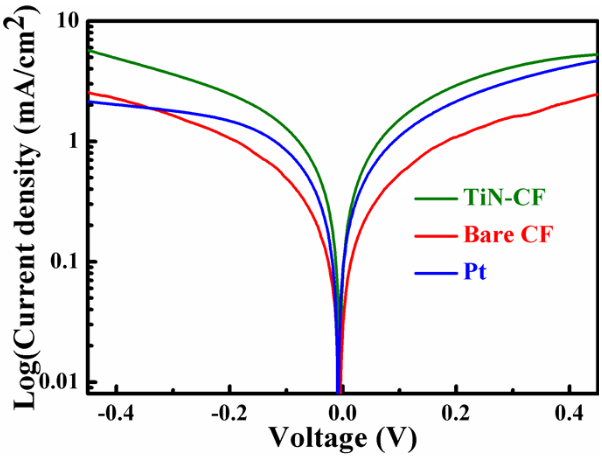

Figure S8. Tafel polarization curves of symmetrical cells fabricated with two identical TiN-CF, Pt wire and bare CF electrodes.

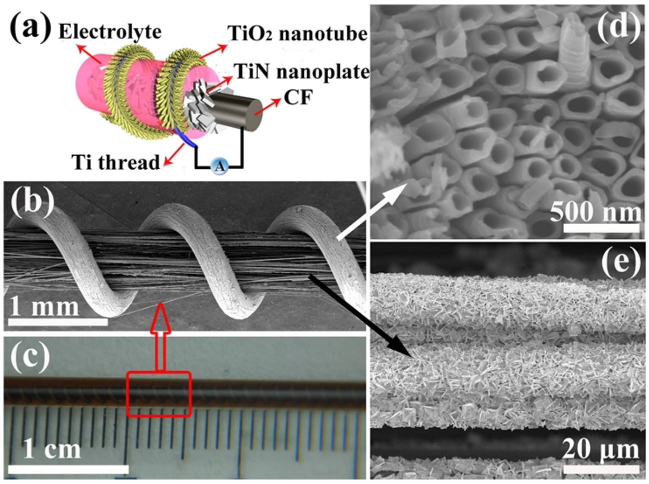

Figure S9. (a) schematic setup of the FDSSC, (b) FE-SEM image of FDSSC, (c) photograph of the FDSSC, (d) FE-SEM image of TiO_2 nanotube growing on Ti thread, and (e) FE-SEM image of TiN nanoplates coating on CF.

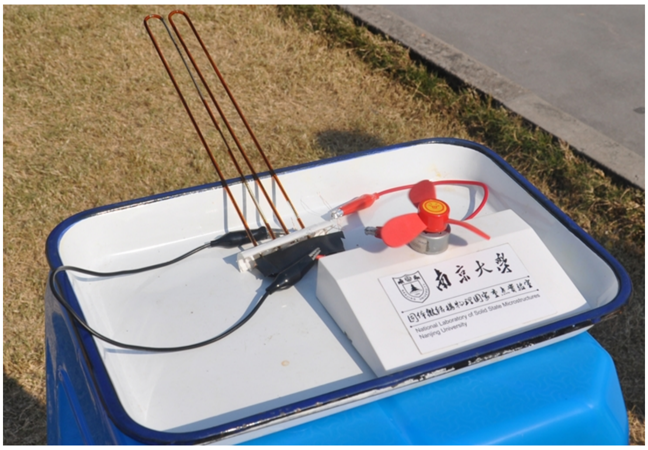

Figure S10. A screenshot of Movie S1 which shows a solar cell module enables to easily drive a small fan motor in an outdoor sunlight.

Supplementary Movie

Movie S1. A four 21cm-long FDSSCs in parallel connection was assembled into a solar cell module, which enables to easily drive a small fan motor in an outdoor sunlight. The electric fan remains running while the cell is under continuous illumination. This movie was taken in Nanjing University (Gulou campus) at 10:00am, Nov. 19, 2013.